

# Composite Solid Ion Conductor with Engineered Lithium Interface

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**Wildcat Discovery Technologies**

**June 24, 2021**

**2021 DOE Vehicle Technologies Office Annual Merit Review**

**Project ID#: BAT479**



This presentation does not contain any proprietary, confidential, or otherwise restricted information

## Timeline:

- Project Start: Oct. 1, 2019
- Project End: Sept. 30, 2021
- % Complete: 79%

## Budget:

Total Project Funding: \$1,529,792

- DOE Share: \$1,223,833
- Wildcat Share: \$305,959
- Funding rec'd for 2019: \$196,538
- Funding rec'd for 2020: \$584,852
- Funding for 2021: \$442,443

## Barriers & Technical Targets:

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost
  - Performance
  - Safety

## Partners:

- None

## Goals:

- Develop a solid polymer-ceramic electrolyte and protected lithium metal anode to enable lithium batteries with energy density greater than 350 Wh/kg with improved safety

## Objectives:

- Develop a composite polymer/ceramic electrolyte using surface modifications to ensure:
  - Low interfacial impedance between the ceramic and the polymer phases
  - Homogeneous dispersion and wetting of the ceramic by the polymer
  - Mechanically stable interfaces
- Develop a coating to mitigate formation of dendrites and high surface area lithium on lithium metal anodes

## Composite SSE Target Properties

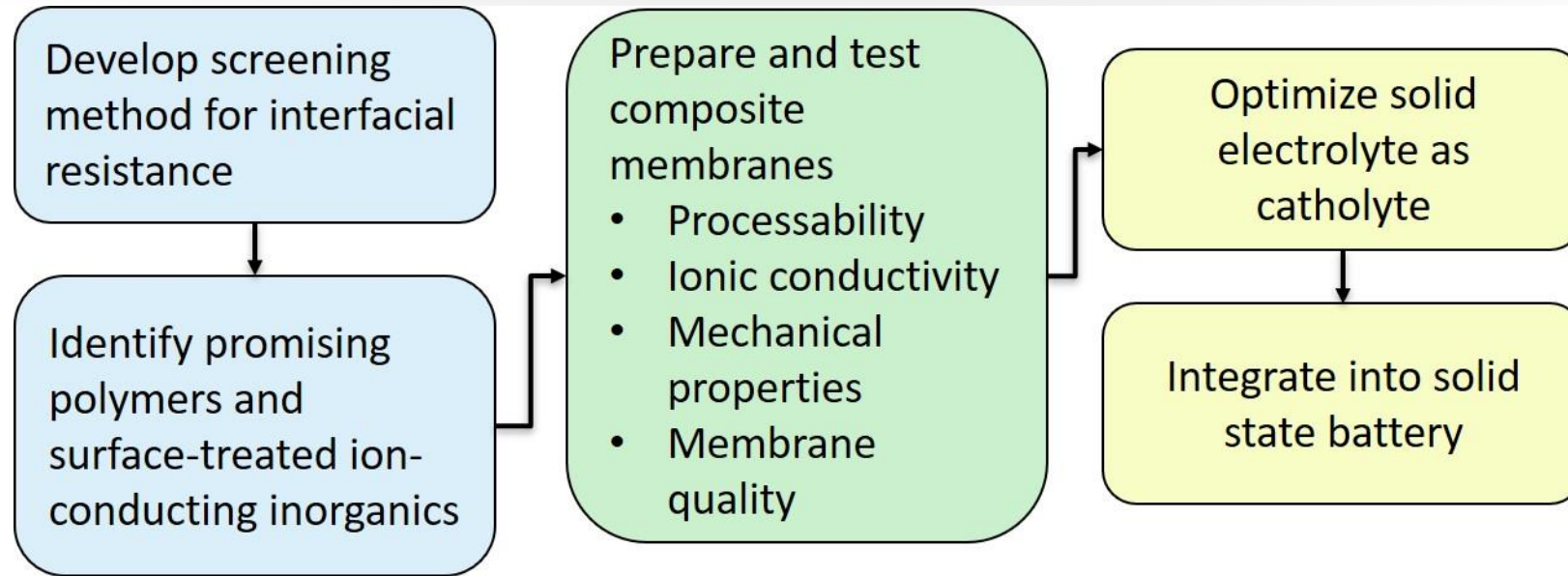
Property	Target
Ionic Conductivity	$\geq 5 \times 10^{-3}$ S/cm
Shear Modulus	$\geq 8.4$ GPa
Oxidative Stability	$\geq 4.3$ V
Lithium Compatibility	Stable
Processability	Standard
Film Thickness	$\leq 20$ $\mu$ m
Thermal Stability	70°C
Low Temperature	-20°C
Cost	< \$10/m <sup>2</sup>

Current Status

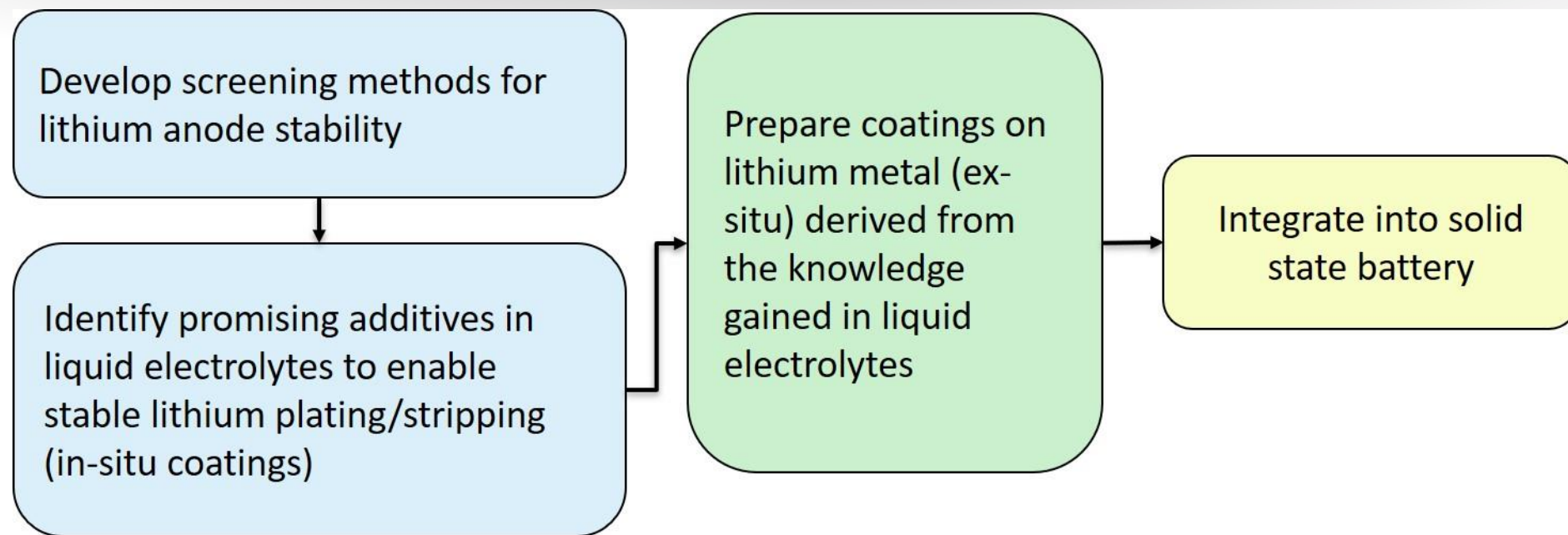
Task	Major Project Tasks	Project Time							
		Y1	Y2					Y3	
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
1.4	Baseline performance established on initial materials	✓							
4.3	Complete synthesis of ceramic ion conductors		✓						
4.4	Down-selection of best ceramic ion conductors for further optimization			✓					
2.6	Down-selection of best composite solid electrolyte additives for further optimization				✓				
3.3	Down-selection of best high voltage polymer formulations for further optimization				✓				
6.3	Down-selection of best approach and materials for lithium passivation					✓			
3.4	Optimization of composite solid electrolyte complete						o		
3.4	Demonstrate polymer oxidative stability > 4.3V on cathode material						✓		
6.2	Final material/process selections complete for final solid state cell optimization and testing							o	
6.5	Final solid-state cell testing results complete								o

✓ = Complete; o = Ongoing

# Approach – Composite Solid Electrolyte



- The use of surface treatments and additives to compatibilize polymers with fillers is widely practiced outside of battery applications
- Focus of project was to apply this concept to composite materials containing polymers and inorganic ion conductors to attain the high conductivity of the inorganic phase with the processability/manufacturability of the polymer phase



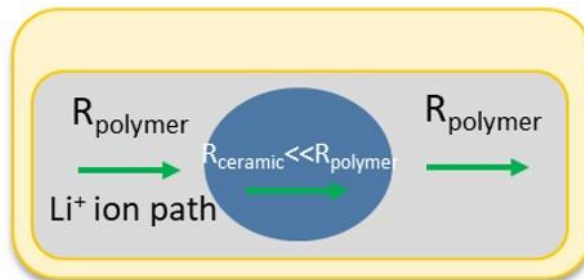
- Screening lithium protection coatings using liquid electrolytes is fast and easy
  - Typical LIB fabrication methods can be used
  - Cells tend to fail fast due to dendrites and SEI formation
- Focus the solid-state battery testing on chemistries that only perform well in liquid electrolytes



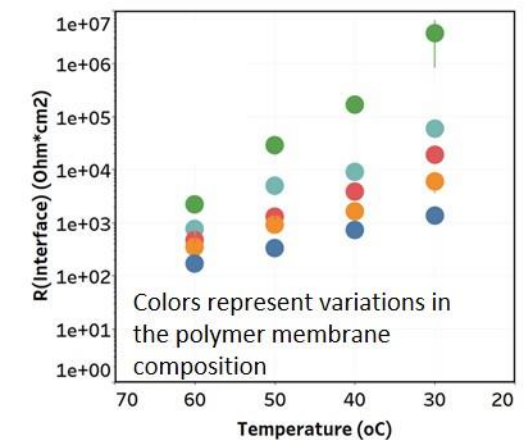
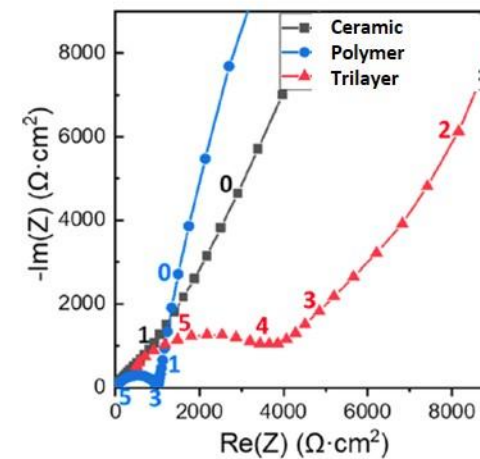
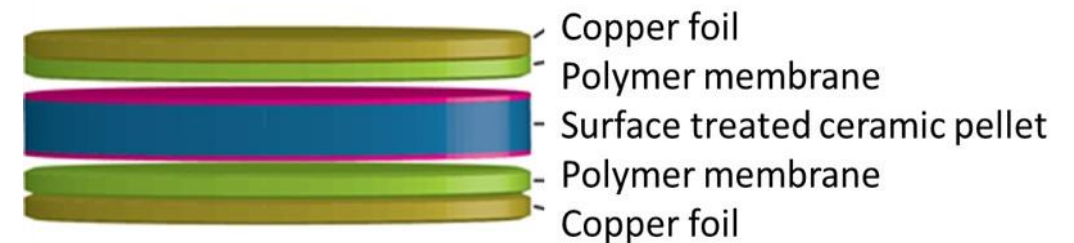
**Objective:** We need to measure the interfacial resistance between the polymer and the ceramic phase

In a composite material, lithium ions need to cross the polymer/ceramic interface repeatedly as they move between cathode and anode

- Need a very low interfacial resistance between the two phases
- Otherwise, the lithium-ion transport will remain in the polymer phase and go around the ceramic particles
- Ion conductivity of the polymer phase is inherently lower than the ceramic



**Accomplishment:** A fast “trilayer” method was developed to provide accurate interfacial resistance values in experimental designs

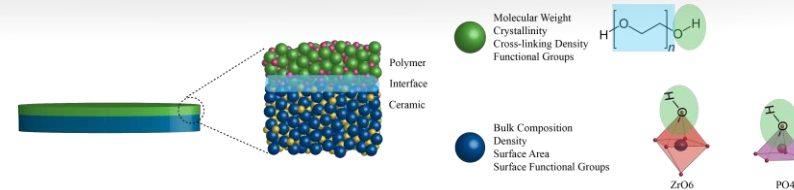


$$R_{\text{Interface}} = (1/2) [R_{\text{trilayer}} - (R_{\text{ceramic}} + R_{\text{polymer}})]$$

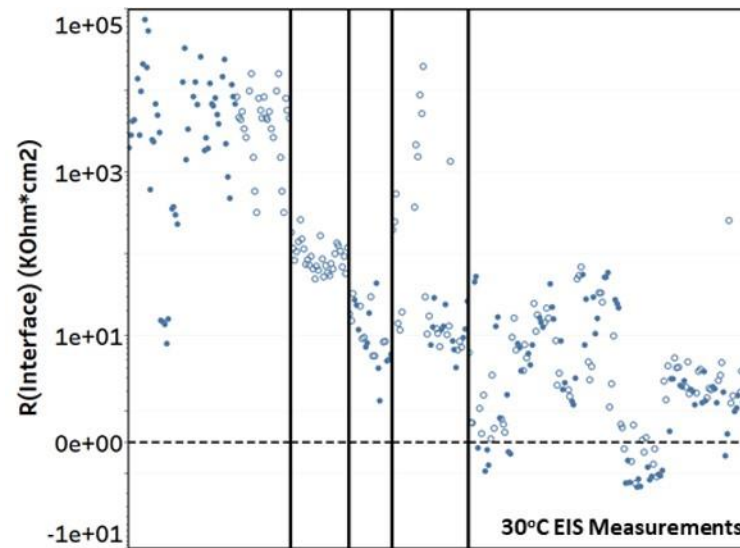
**Objective:** Demonstrated that we can reduce or eliminate the interfacial resistance between the two phases

**Accomplishments:** Interfacial resistance can be significantly reduced with appropriate surface treatments and material combinations

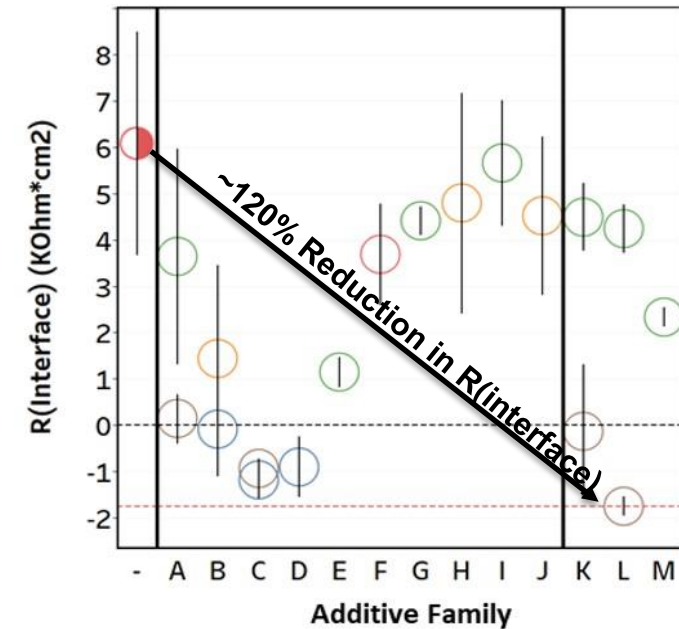
- Solutions are not obvious
- Chemistry trends can be identified and used to seek further improvements
- Effect was validated for multiple polymer/ceramic systems



$$R_{interface} = \left(\frac{1}{2}\right) [R_{Trilayer} - (R_{GF} + R_{Polymer})]$$



Over 5200 EIS Measurements Run!



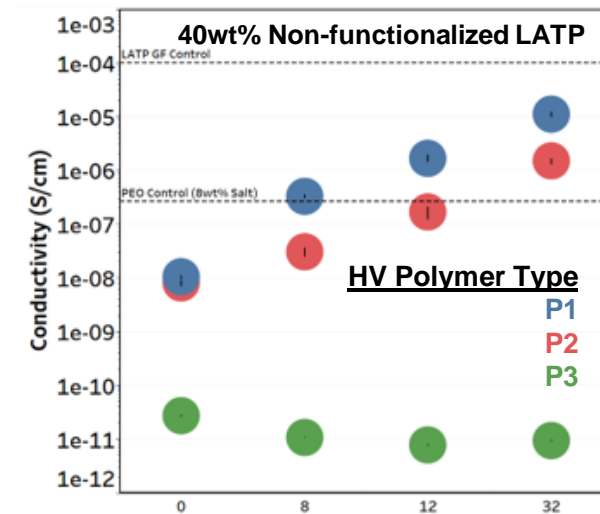
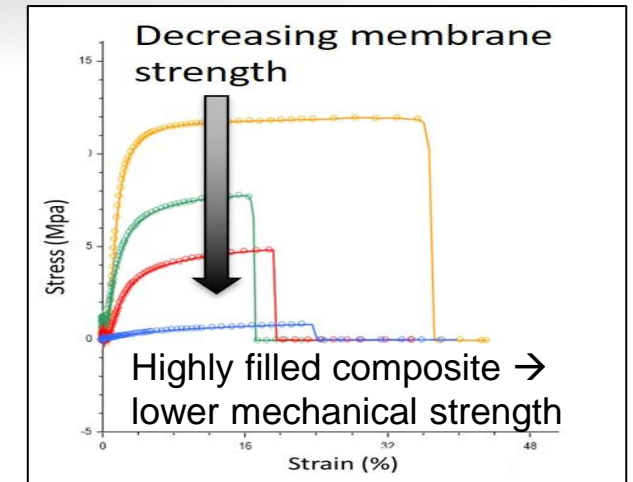
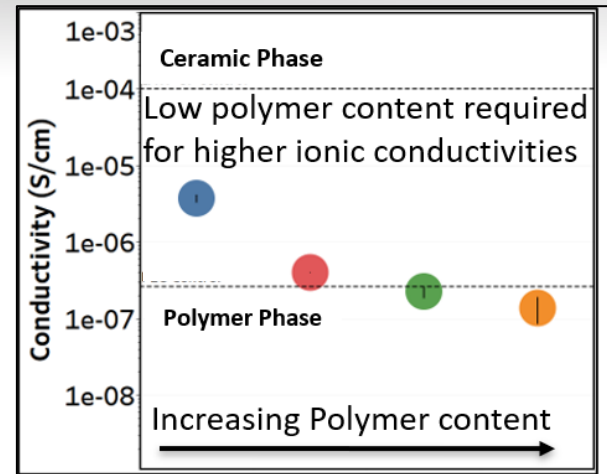
Coupling agents identified for multiple polymer/inorganic systems to significantly reduce interfacial resistance



**Objective:** Produce a polymer/ceramic composite with low interfacial impedance between the two phases to achieve ionic conductivity similar to that of the inorganic

**Accomplishments:** Identified compositional ranges required to achieve ionic conductivities similar to that of the inorganic material

- Ultimate ionic conductivity is limited by that of the inorganic material
- Needs to be a “highly filled” polymer composite
- Membrane needs to be primarily inorganic material with polymer serving as a binder
- Mechanical strength of membrane decreases unless the interaction between the polymer and the inorganic is very strong

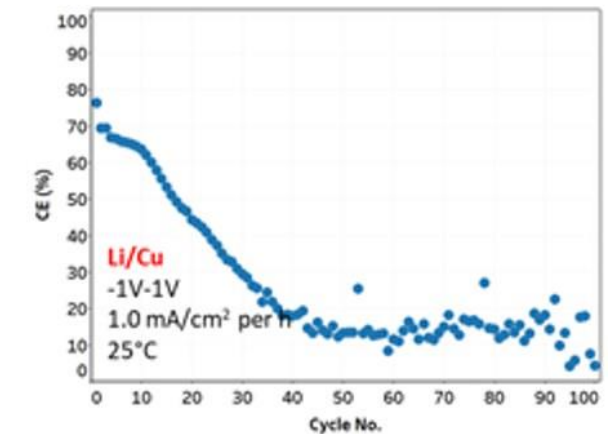
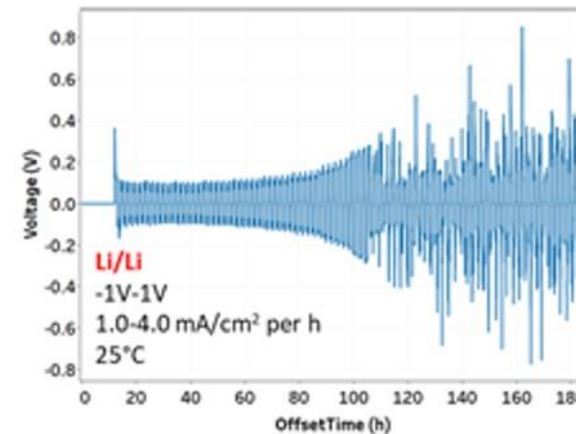
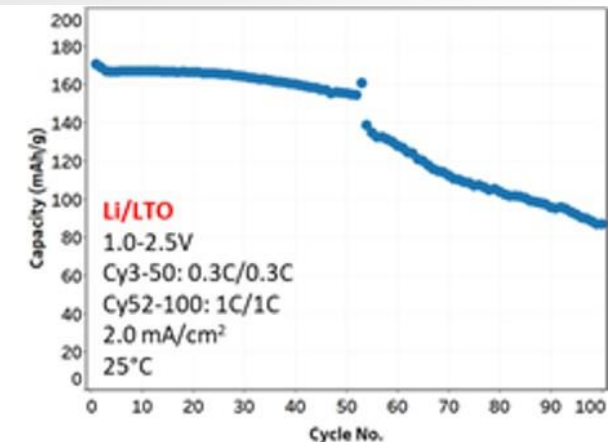
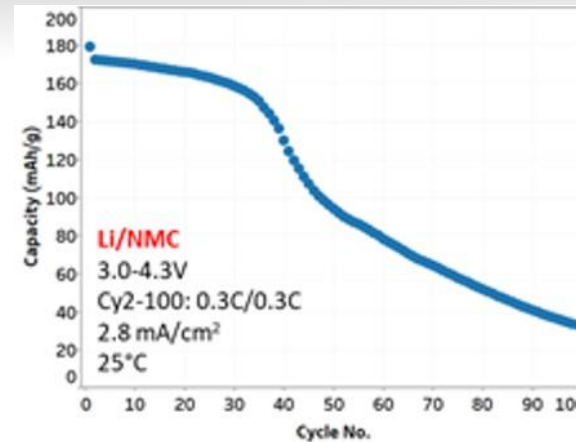


Identified composite compositions that yield improved conductivities, but need to improve mechanical strength

**Objective:** We need a fast, accurate screening method to evaluate lithium metal protection coatings using liquid electrolyte

**Accomplishments:** Evaluated multiple material combinations for fast electrochemical evaluation of lithium metal protection coatings

- NMC//Li is ultimate chemistry and can be used to evaluate voltage stability of the composite solid-state electrolyte
- Alternative pairings such as LTO minimize effects from higher voltage cathodes

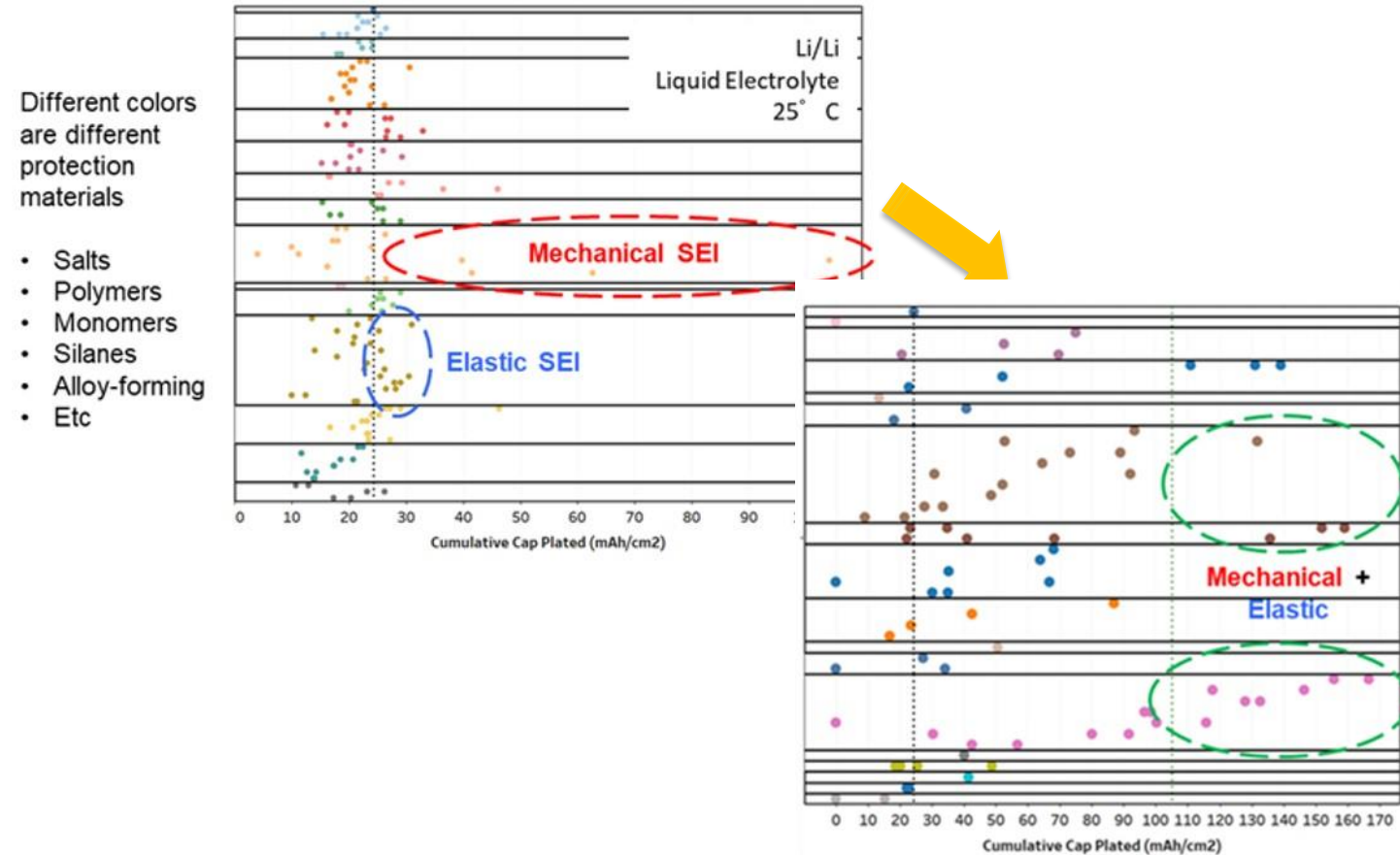


Li//Li symmetric cells selected to monitor both Li stripping and plating behavior

**Objective:** Identify coating chemistries using liquid electrolyte additives that yield good performance

**Accomplishments:** Identified several chemical approaches for lithium protection.

- Significant improvement in cumulative capacity plated prior to failure for specific chemistries
- SEI benefits for specific chemistries were then combined to achieve even better performance

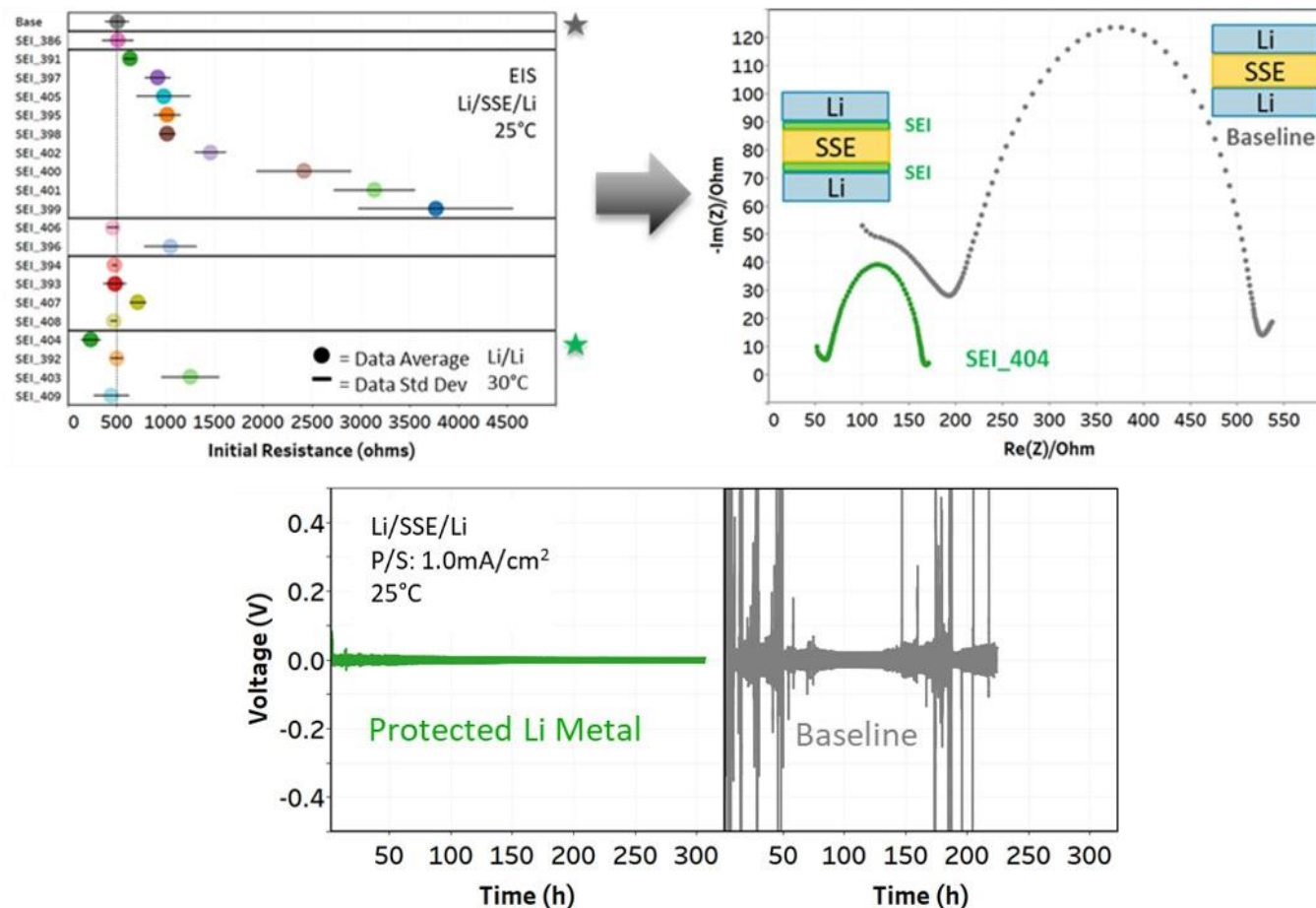


Combinations of coating chemistries yielded the biggest improvements in cumulative capacity plated

**Objective:** Translate approaches identified using liquid electrolytes to solid state electrolytes

**Accomplishments:** Demonstrated stable lithium plating/stripping in symmetric cells containing composite solid electrolyte

- Identified the lithium metal coatings with lowest initial resistance in the Li//Li cell
- Significant reduction relative to resistance with non-coated lithium metal
- Stable cycling in symmetric cell achieved



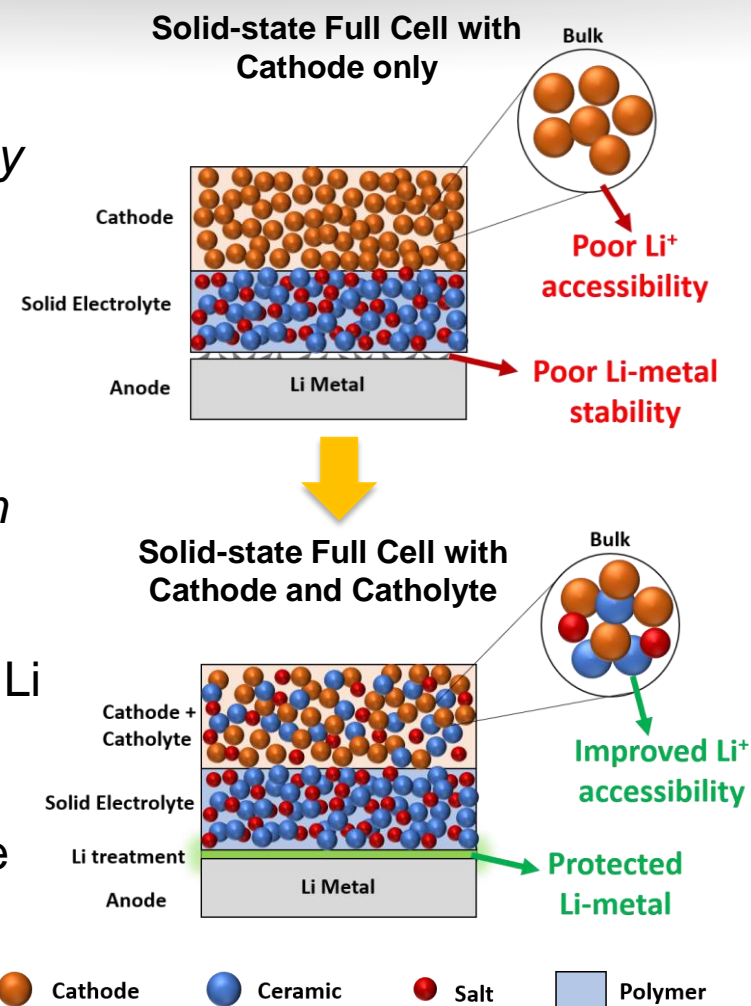
Translating the protection methods from liquid to SSE was effective



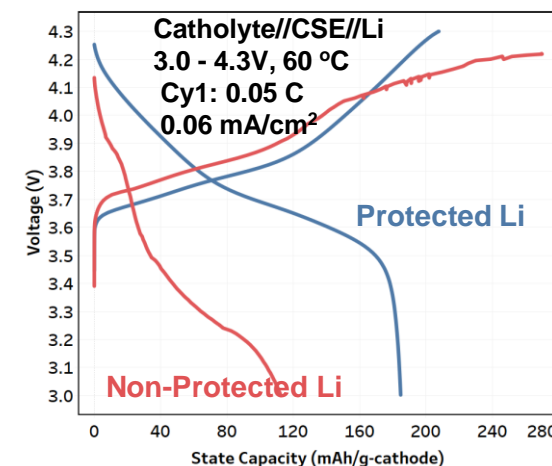
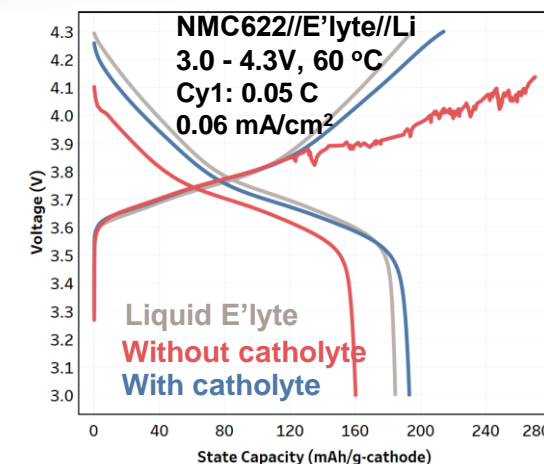
**Objective:** Demonstrate all-solid-state cells by integrating composite solid electrolytes (CSE) and lithium metal protection with a suitable cathode-catholyte composition

**Accomplishments:** Assembled all-solid-state Li//NMC full cells with an NMC cathode and an NMC cathode-catholyte composition

- Developed an NCM-based solid-state cells that could charge up to 4.3V with protected Li metal anode
- Li//NMC full cell with catholyte incorporated into the cathode was chosen as test-vehicle for full-cell development



Cy1 Trace of Solid-state Full Cells



Li//NMC-catholyte cells were chosen as the test vehicles to evaluate all-solid-state cells' performance

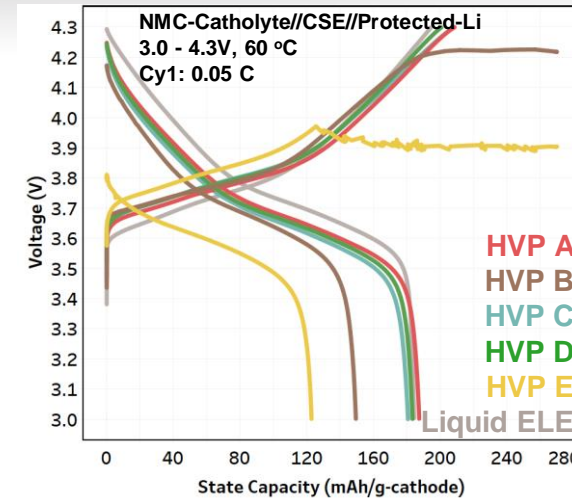


**Objective:** 1) To screen catholyte compositions and integrate it with optimized composite solid electrolyte (CSE) and to identify the parameters that affect the solid-state full-cell's ability to deliver a full charge up to 4.3V and the cycling performance

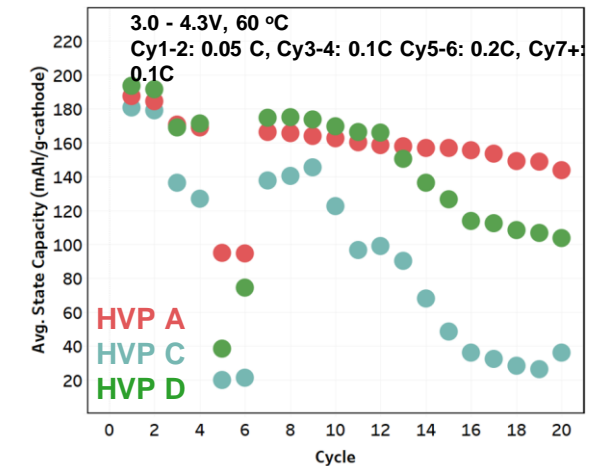
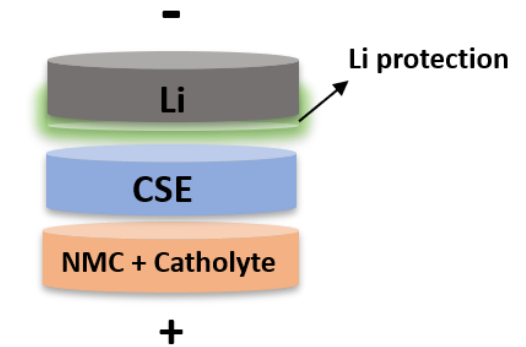
**Accomplishments:**

- High-throughput screening allowed simultaneous evaluation of multiple CSE and High Voltage Polymer (HVP) candidates in Li//NMC catholyte full cell configuration
- We found that the **HVP type in the CSE** plays an influential role in the full-cell's ability to charge up to 4.3 V and the its discharge capacities
- We narrowed down HVP candidates for further optimization in full cells

Full cells with different CSE-HVPs



Cell Configuration



HVP types and CSE compositions that can consistently deliver a full charge up to 4.3V were identified

# Response to Previous Year's Reviewers' Comments

- This is the first year that the project has been reviewed

- No outside collaborations occurred on this project

- Composite SSE approach should be general
  - Should identify coupling agents/surface treatments for a variety of polymer/inorganic combinations
- Production of highly filled inorganic composites with good mechanical strength is challenging
  - Should be achievable as other industries use these (EM shielding, thermal, and optical applications)
- Interfacial resistance within cathode still needs to be reduced
  - Wildcat focused on reducing interfacial resistance within the SSE composite
- Consistent, low-cost source of thin lithium is needed

- Composite SSE
  - Wildcat is still building on database of coupling agents/surface treatments for more combinations of polymers and inorganic ion conductors
  - Optimize incorporation of the SSE (catholyte) into the cathode
- Protected lithium anode
  - Further reduce resistance between SSE and coated lithium
  - Continue to build database of chemistry vs. performance for further knowledge and improvements

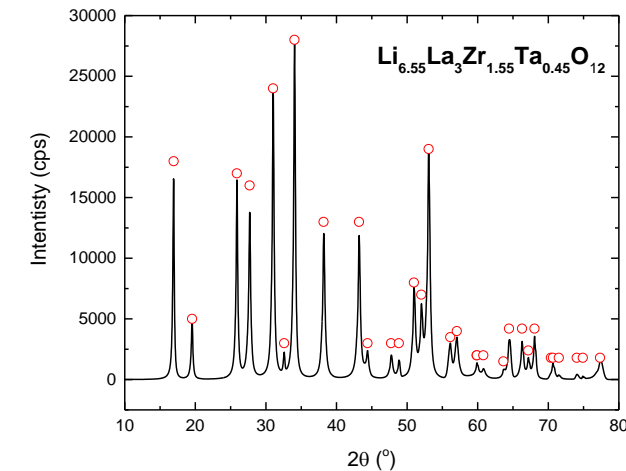
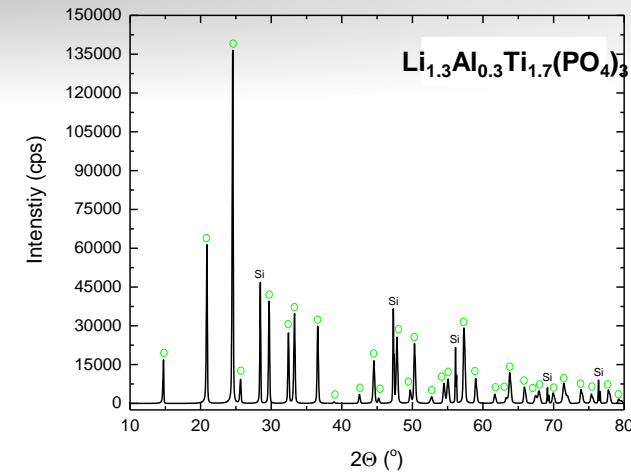
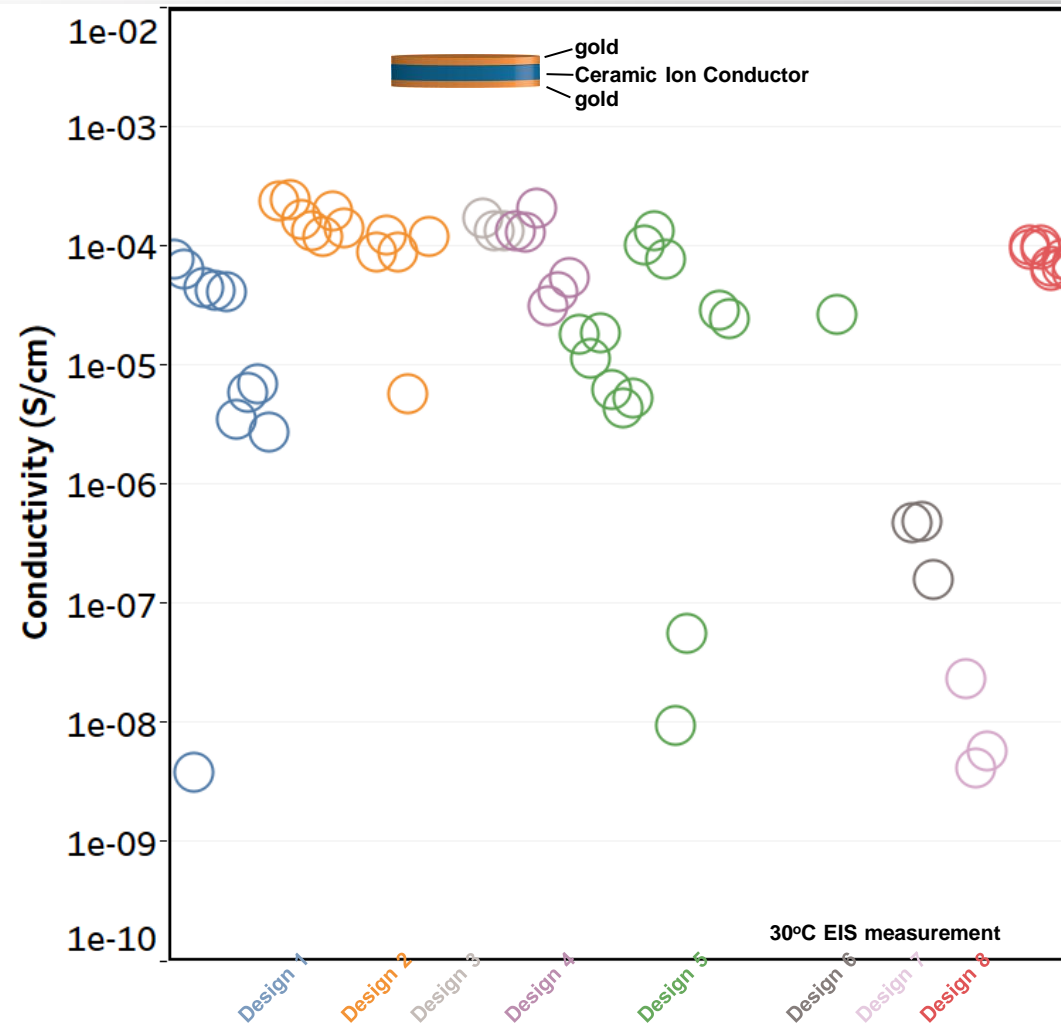
Any proposed future work is subject to change based on funding levels



- **Thrust 1 (Composite Solid Electrolyte)**
  - Screened many coupling agents/surface treatments at various of polymer/ceramic composite system using Wildcat Tri-layer test vehicle → Over 5,200 EIS measurements have been done
  - Successful demonstration of significant interface resistance reduction in Tri-layer system showed great promise for implementing effective surface treatments to composite solid electrolyte development
  - Greatly improved the composite solid electrolyte film quality with reasonable amount of ceramic
- **Thrust 2 (Li-metal)**
  - Screened many of surface coatings to protect Li metal surface
  - Successfully identified several promising coatings with much improved total Li stripping/plating capacity
- **Thrust 3 (All Solid-State Full cell)**
  - Developed and tested catholyte composites in full cell using composite solid electrolyte from Thrust 1 and protected Li metal surface from Thrust 2
  - Demonstrated working all solid-state cell with no liquid components with reasonably good cycle life

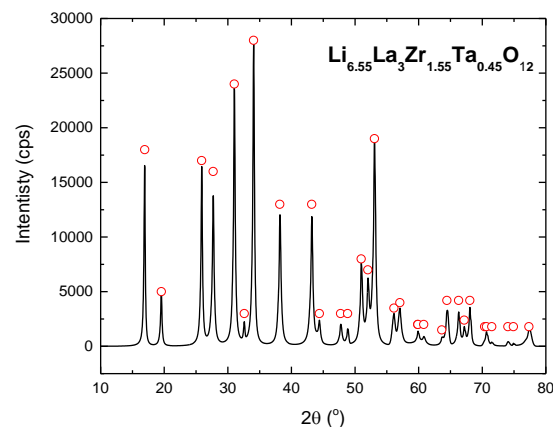
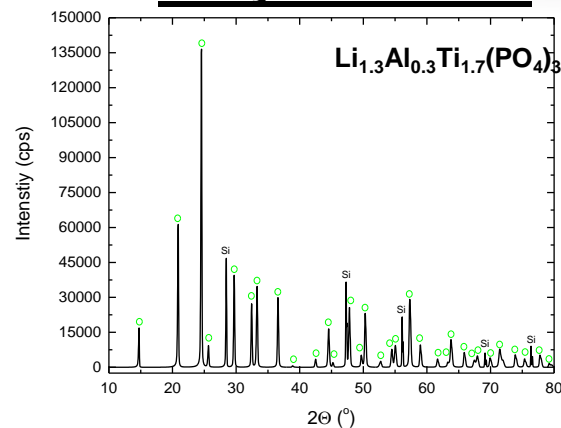
## Technical Back-up Slides

# Synthesis Optimization of Ceramic Ion Conductors

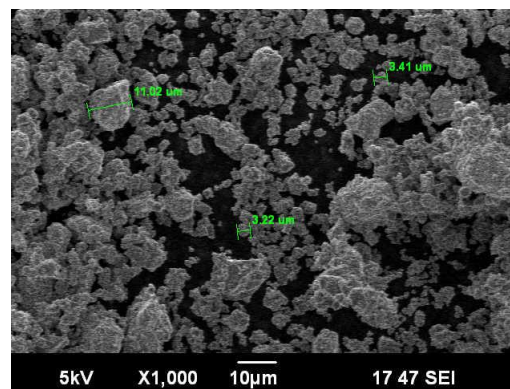
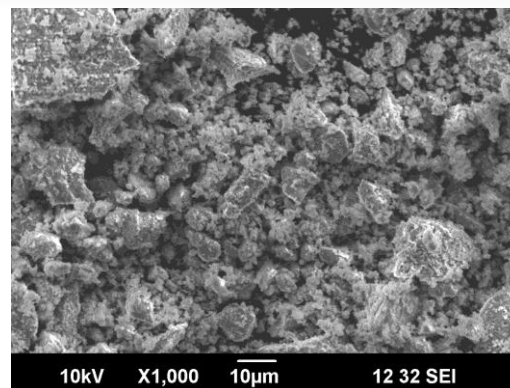


Wildcat HT synthesis enables rapid screening of ceramic ion conductors

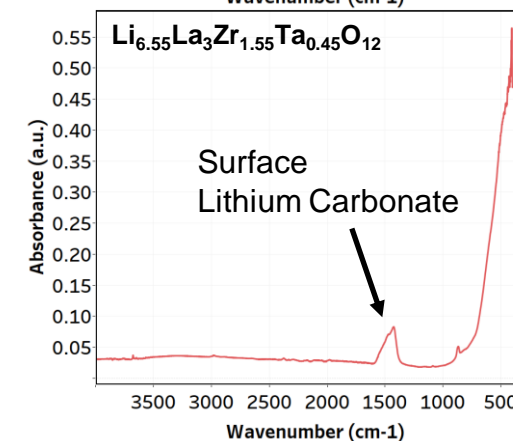
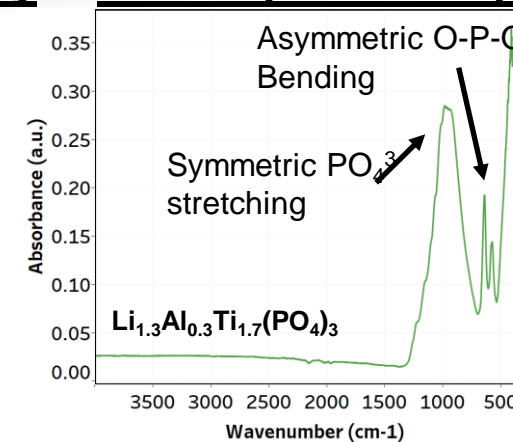
## X-ray Diffraction



## Scanning Electron Microscopy



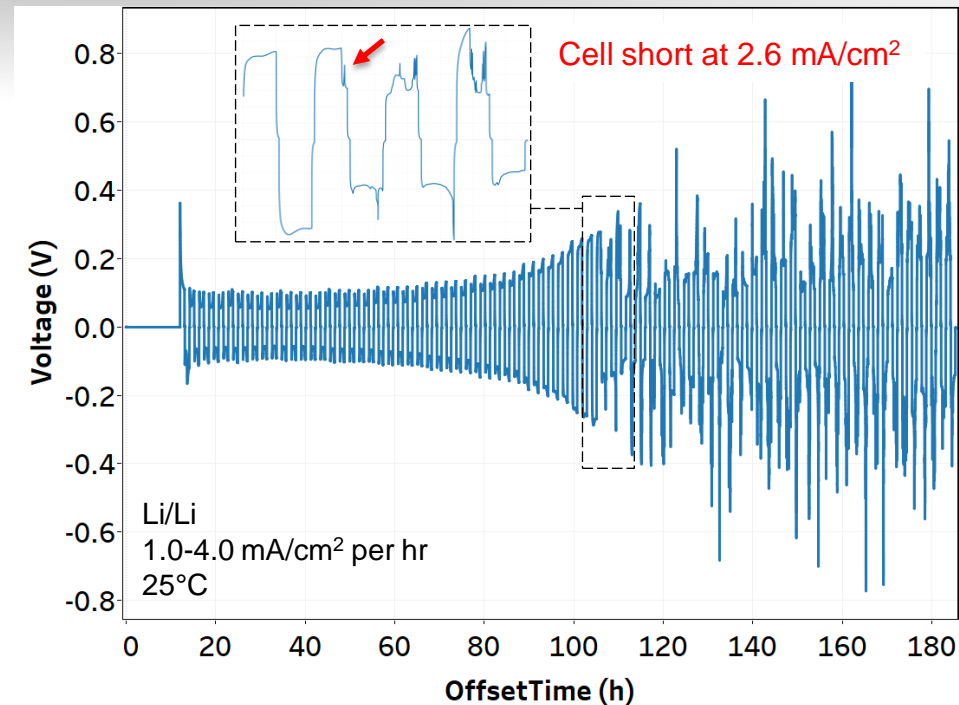
## FT-IR Spectroscopy



Down-selection of LATP as an air stable ceramic ion Conductor

# Li/Li cells: Cycling protocol, Cell failure example

Cycle No.	Plating/Stripping Current Density (mA/cm <sup>2</sup> , for 1hr)	Theor. Li Deposited (μm)
1-5	1.0	4.82
6-10	1.2	5.78
11-15	1.4	6.75
16-20	1.6	7.71
21-25	1.8	8.68
26-30	2.0	9.64
31-35	2.2	10.60
36-40	2.4	11.57
41-45	2.6	12.53
46-50	2.8	13.50
51-55	3.0	14.46
56-80	3.2-4.0	15.42-19.38



- When using Li//Li symmetric cell format, an increasingly aggressive cycling protocol will be used (Increasing current density from 1.0-4.0 mA/cm<sup>2</sup>)
- Example Li//Li cycling performance is shown on the right
- A soft short occurs when a current density of 2.6 mA/cm<sup>2</sup> is reached (red arrow)

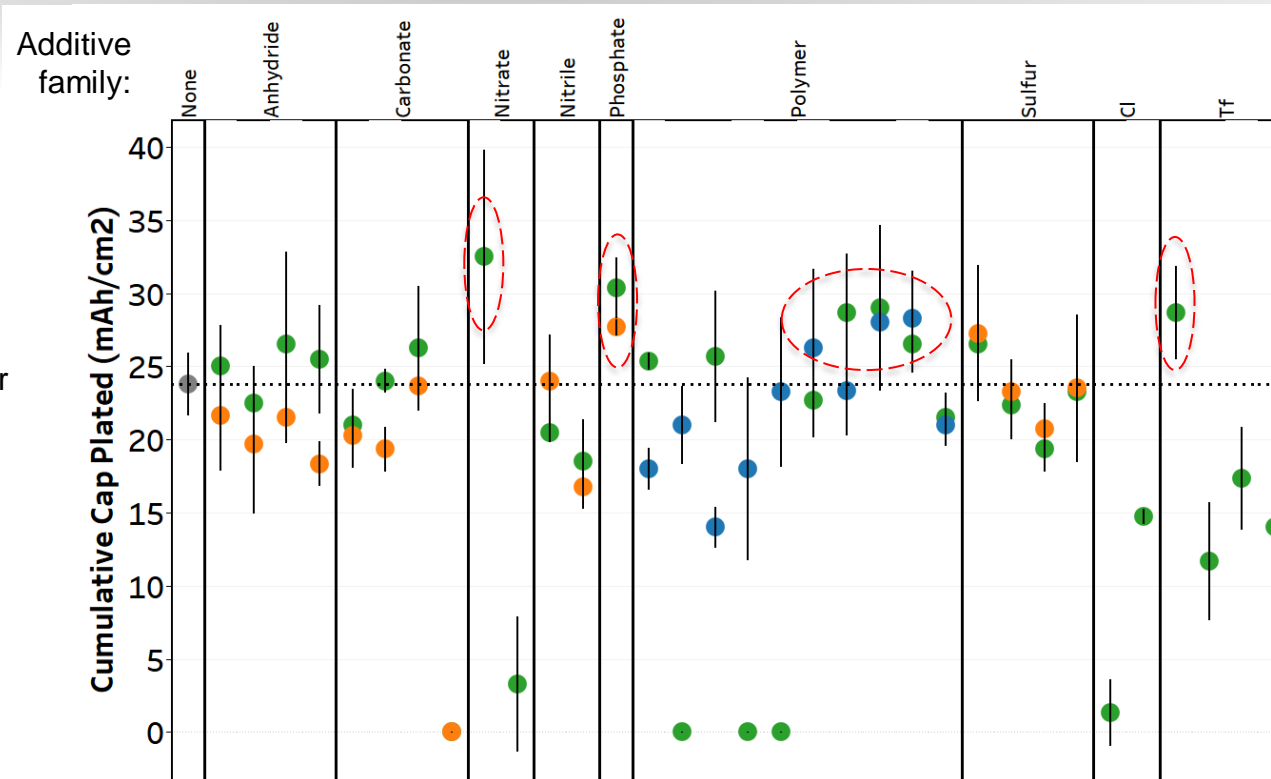


# Li/Li Cells: Initial Single Additive HT Screening

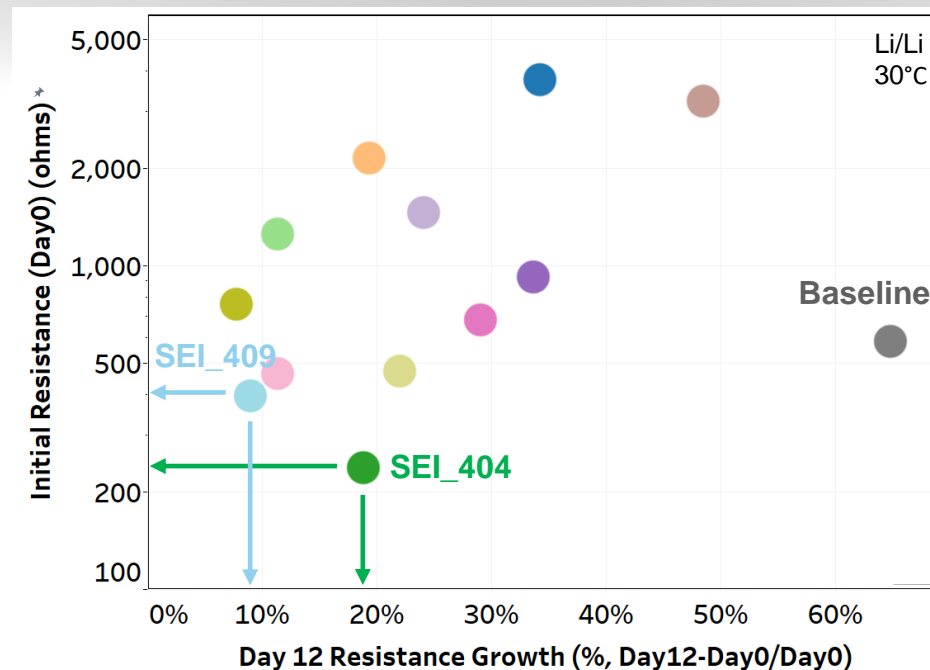
Li/Li  
Li thickness: 20 $\mu$ m  
Elyte amount: Lean  
P/S: 1.0 mA/cm<sup>2</sup>, 1hr  
25 °C

Treatment Conc

Low  
Med  
High



- Many types of additives families are currently being tested and compared to a baseline (non-treated Li metal) system
- While many of these additives show worse/comparable performance to the baseline system, some (red circle) are showing promising performance



- To determine the ability of the Li metal protection to prevent resistance growth due to SSE decomposition, calendar life testing is performed
- Compared to the baseline system, many Li metal protections showed minimalized resistance growth but also showed higher initial resistance
- Among them, SEI 404 and 409 showed the most promising results in terms of both initial resistance and resistance growth